

PCT

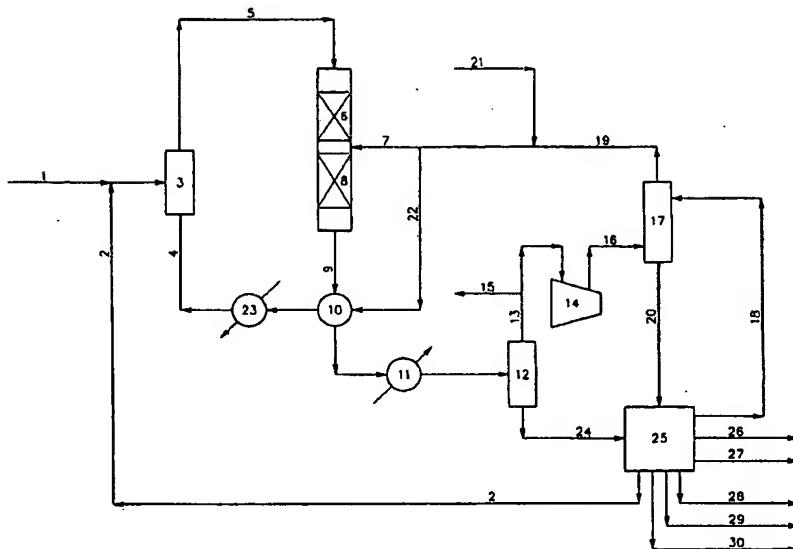
WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>6</sup> :	A1	(11) International Publication Number:	WO 99/35136
C07D 307/08, 307/32		(43) International Publication Date:	15 July 1999 (15.07.99)
(21) International Application Number:	PCT/EP99/00013	(81) Designated States:	AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
(22) International Filing Date:	5 January 1999 (05.01.99)	(30) Priority Data:	9800013 8 January 1998 (08.01.98) BE
(71) Applicant (for all designated States except US):	EURODIOL S.A. [BE/BE]; Parc Industriel Zone A, B-7181 Feluy (BE).	(72) Inventor; and	
(75) Inventor/Applicant (for US only):	BERTOLA, Aldo [IT/IT]; Via Luigi Illica, 5, I-20121 Milano (IT).	(74) Agent:	SARPI, Maurizio; Studio Ferrario, Via Collina, 36, I-00187 Roma (IT).

(54) Title: PROCESS FOR THE PRODUCTION OF TETRAHYDROFURAN AND GAMMABUTYROLACTONE



(57) Abstract

A process for the production of tetrahydrofuran and gammabutyrolactone from maleic, succinic anhydride or fumaric acid esters, by vapour phase hydrogenation in two subsequent stages, the former on a copper based catalyst, the latter on an acid silica rich silica-alumina type catalyst.

BEST AVAILABLE COPY

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LK	Liberia	SG	Singapore		
EE	Estonia						

Process for the production of Tetrahydrofuran and Gammabutyrolactone.

DESCRIPTION

The present invention relates to a process for the production of tetrahydrofuran and gammabutyrolactone, particularly to a process starting from maleic, succinic anhydride or fumaric acid esters, 5 by vapour phase hydrogenation in two subsequent stages, the former on a copper based catalyst, the latter on an acid silica rich silica-alumina type catalyst.

Tetrahydrofuran is a solvent used extensively in organic chemistry, and on the industrial scale it is 10 in high demand for the production of natural and synthetic resins. Gamma-butyrolactone is on the other hand among the other things a useful solvent for acrylate and styrene polymers.

It is known from the prior art that there 15 exist several methodologies that can be employed for the production of Tetrahydrofuran (THF) and Gammabutyrolactone (GBL).

THF is produced starting from BDO, by a process involving dehydration. GBL too is produced 20 starting from BDO by a process involving dehydrogenation. The production of THF and GBL starting from BDO is particularly costly because of the relatively high costs inherent with BDO, whose production involves rather complex processes.

25 According to a method which is widely utilised by industry, BDO is produced allowing acetylene to react with formaldehyde, with concomitant

formation of butynediol which subsequently undergoes hydrogenation to form BDO.

Mitsubishi Chemical Industries of Japan has developed a process for the production of BDO starting 5 from Butadiene.

The synthetic strategy comprises butadiene acetoxylation to 1,4-diacetoxyl-2-butene, which is subsequently hydrogenated and hydrolysed to BDO.

General Electric Corporation patented a 10 process for the production of BDO starting from propylene. The synthetic pathway in this case includes conversion of propylene to allyl acetate, subsequently converted to 4-acetoxylbutanol which forms BDO after hydrolysis.

15 Special attention has been devoted to the development of processes in which butane is utilised as starting material, through the formation of a maleic anhydride intermediate.

Several processes have been proposed for the 20 production of THF, GBL or BDO starting from maleic anhydride, its esters or similar esters like succinic and/or fumaric acid esters.

US Patents N° 4,584,419 and 4,751,334 assigned to Davy McKee Ltd. describe processes for the 25 production of BDO by hydrogenation of carboxylic acid esters that contain 4 Carbon atoms (typically ethyl maleate).

In International Patent WO 86/07358, this too assigned to Davy Mc Kee Ltd, an account is given for a 30 process where GBL is produced starting from maleic

anhydride or the homologous dicarboxylic acid esters, by hydrogenation carried out in the vapour phase and in two subsequent stages on a chromite type catalyst.

In EP N°322 140 in the name of Standard Oil Company, a process for the production of THF and GBL is given, starting from maleic or succinic anhydride, by a single stage hydrogenation on a catalyst made up of a copper, zinc and aluminium based mixture.

Aim of the present invention is to propose a process for the production of THF and GBL in varying proportions, starting from maleic anhydride and/or succinic acid and/or fumaric acid esters, all of these obtained allowing the acids or anhydrides thereof to react with an alcohol containing from 1 to 4 Carbon atoms.

According to the present invention the process is based on the production of tetrahydrofuran and gammabutyrolactone, by vapour phase selective hydrogenation of maleic anhydride, succinic anhydride and/or fumaric acid esters, characterised by the fact that the hydrogenation takes place in two subsequent stages, of which the former takes place on a copper based catalyst, and the latter on an acidic silica-alumina type catalyst that is rich in silica.

These and other features will be more readily apparent from the following description of a preferred not limiting embodiment of the invention with reference to the accompanying drawing in which a scheme of the production process is shown.

In the process object of the present

invention the ester, after being completely vapourised by a hydrogen rich stream, is fed to a reactor characterised by two distinct reaction stages. The first stage contains a copper based heterogeneous 5 hydrogenation catalyst, with a preference given to copper -zinc oxide or stabilised copper chromite type catalysts.

The subsequent reaction stage contains an acidic silica enriched silica-alumina type 10 heterogeneous catalyst.

To allow the reaction to take place in the vapour phase, the reaction mixture must be very rich in hydrogen.

The hydrogen to ester molar ratio ranges 15 between 100 and 600, preferably between 200 and 400.

Pressure and temperature as well as catalyst contact times in each reaction stage may be optimised depending on the choice of the GBL:THF product ratio. Such ratio may be varied within a wide range, that is 20 GBL:THF ratios that go from 70:30 to 40:60.

The average operating pressure ranges between 3 and 40 bars, preferably from 15 to 25 bars.

In both reaction stages, temperatures range between 180 and 280 °C, and typically between 200 and 25 250°C.

Overall Liquid Hourly Space Velocity ranges between 0.1 and 0.5 hr<sup>-1</sup>.

The space velocity with which the gaseous mixture goes on the catalyst (gaseous space velocity on 30 the catalyst) in the second reaction stage results to

be 1.5 to 10 times higher than that on the catalyst of the first reaction stage.

A cooling between the first and second reaction stage can be carried out in a heat exchanger 5 or more simply by mixing the cold hydrogen mixture to the effluent in the first reaction stage.

A typical process scheme is shown in the enclosed drawing.

Operating conditions refer to a starting 10 material consisting of dimethylsuccinate (DMS).

The process is essentially feasible even in case the starting material consists of carboxylic acid esters with 4 Carbon atoms.

The ester feedstock (Line 1) is fed to 15 vapouriser 3 together with a recycle stream (line 2) that contains BDO and unconverted DMS, from product fractionation unit 25.

The recycle stream usually includes GBL which yields an azeotropic mixture with DMS.

In vapouriser 3, the feed (Line 5) and the 20 recycle (Line 2), come in contact with a hot hydrogen stream (Line 4), and they vapourise.

In the gas stream from the vapouriser (Line 5) the Hydrogen:shot molar ratio is 200, temperature is 25 210 °C, pressure is 15 ATE.

Such stream feeds the first stage of reaction 6 which contains a copper-zinc oxide type catalyst.

Temperature at the outlet of the first stage is taken down from approx 225°C to approx. 200°C by 30 injection of a cold hydrogen stream (Line 7).

In the second stage of reaction 8, gases flow on an acidic silica-alumina type catalyst rich in silica.

A catalyst employed in the process is an 5 acidic mordenite or zeolite, with an ABD apparent density of 0.65 and surface area equalling 450 m<sup>2</sup>gr<sup>-1</sup>.

At the outlet of the second rection stage, the overall conversion is as high as 97%, with the following product yields:

10	GBL	53%
	THF	34%
	BDO	7%
	Byproducts	3%

Liquid Hourly Space Velocity is as high as 15 0.2 hr<sup>-1</sup>.

The effluent from the second stage of reaction (line 9) cools down in exchanger 10 giving heat to the recycle hydrogen rich stream, and in exchanger 11, to eventually feed separator 12, where 20 the condensed organic phase separates from the hydrogen rich gaseous phase.

The gaseous phase at the outlet of separator 12 (Line 13) is compressed by compressor 14, to be recycled to the reaction system.

25 A fraction of the recycle gas is purged (line 15) to hinder deposition of inert materials.

Compressed gas (line 16) feeds column 17, where it comes to contact with a GBL rich stream (line 18) that comes from product fractionation unit 25.

30 Recycle gases are washed with a GBL rich

stream, and this allows the vapour phase present in the gases to be effectively removed.

As known, water is a by-product of THF synthesis. An efficient removal of water, as that obtained washing the recycle gas with a GBL enriched liquid stream, is important to avoid deterioration of the copper based catalyst.

After the wash, the GBL enriched stream (line 20) gets back to by-product fractionation unit 25, 10 where the water which had been previously absorbed is removed.

Dried gases (line 19), together with the hydrogen feed (line 21) partly (line 7) mix with the effluents from Stage 1 of reactor 6 and partly (line 15 22) preheat in exchanger 23, to eventually feed vapouriser 3.

The liquid phase at the outlet of separator 12 feeds (line 24) a product fractionation unit 25, where THF (line 26), methanol (line 27), GBL (line 28), 20 a fraction containing BDO and DMS which is recycled to the reaction (line 2), heavy organic byproducts (line 29), water and light organic byproducts (line 30) are separated.

The entire process allows direct and simple 25 production of GBL and THF, with a high degree of flexibility, avoiding all the complications which are proper of other production processes, where GBL and THF are produced employing BDO as starting material.

## CLAIMS

1. A process for the production of tetrahydrofuran and gammabutyrolactone, by vapour phase selective hydrogenation of maleic anhydride, succinic anhydride and/or fumaric acid esters, characterised by the fact that the hydrogenation takes place in two subsequent stages, of which the former takes place on a copper based catalyst, and the latter on an acidic silica-alumina type catalyst that is rich in silica.
- 10 2. A process according to claim 1, characterised by the fact that the ester alkyl component contains from 1 to 4 carbon atoms.
- 15 3. A process according to claims 1 and 2 characterised by the fact that the hydrogenation operating pressure ranges between 3 and 40 bars, and operating temperature ranges between 180 and 280 °C.
- 20 4. A process according to claims 1,2,3 characterised in that the hydrogenation operating pressure ranges between 15 and 25 bars.
5. A process according to claims 1,2,3 characterised by the fact that the hydrogen to ester ratio in the reactor shot ranges between 100 and 600.
- 25 6. A process according to claim 4, characterised in that the hydrogen to ester shot ratio in the reactor ranges between 200 and 400.
7. A process according to claims 1,2, and 3 characterised in that the GBL to THF ratio ranges between 70/30 and 40/60.
- 30 8. A process according to claim 1, characterised in that in the first hydrogenation

stage the catalyst is copper-zinc oxide or of the copper chromite type and it is coupled in the second stage with a catalyst rich in silica.

9. A process according to claim 1 wherein a catalyst employed in the second stage is an acidic mordenite or zeolite.

10. A process according to claim 8, characterised in that the copper chromite is stabilised.

11. A process according to claim 5, characterised by the fact that in the second stage the catalyst has a specific surface area ranging between 50 and 800  $\text{m}^2\text{g}^{-1}$ .

12. A process according to claim 9 wherein the ABD apparent density of the catalyst is 0.65 and its surface area equals 450  $\text{m}^2\text{gr}^{-1}$

13. A process according to claims 1, 8 and 9 characterised by the fact that catalyst in the second stage contains between 80 and 100 % silica.

14. A process according to claims 1, 8, 11 and 12 characterised by the fact that the vapour phase mixture containing hydrogen and ester flows on the catalysts with a liquid hourly space velocity that ranges between 0.1 and 0.5  $\text{hr}^{-1}$ .

15. A process according to claims 1, 8 11, 12 and 14 characterised by the fact that the vapour phase travels on the reaction second stage catalyst with a space velocity which is 1.5 to 10 times higher than that on the catalyst of the reaction first stage.

16. A process according to claims 1 and 2,

characterised by the fact that the hydrogen rich recycle stream is washed downstream from the reaction with a butyrolactone rich stream, to remove the steam present in the recycle gas.

5

10

15

20

25

30

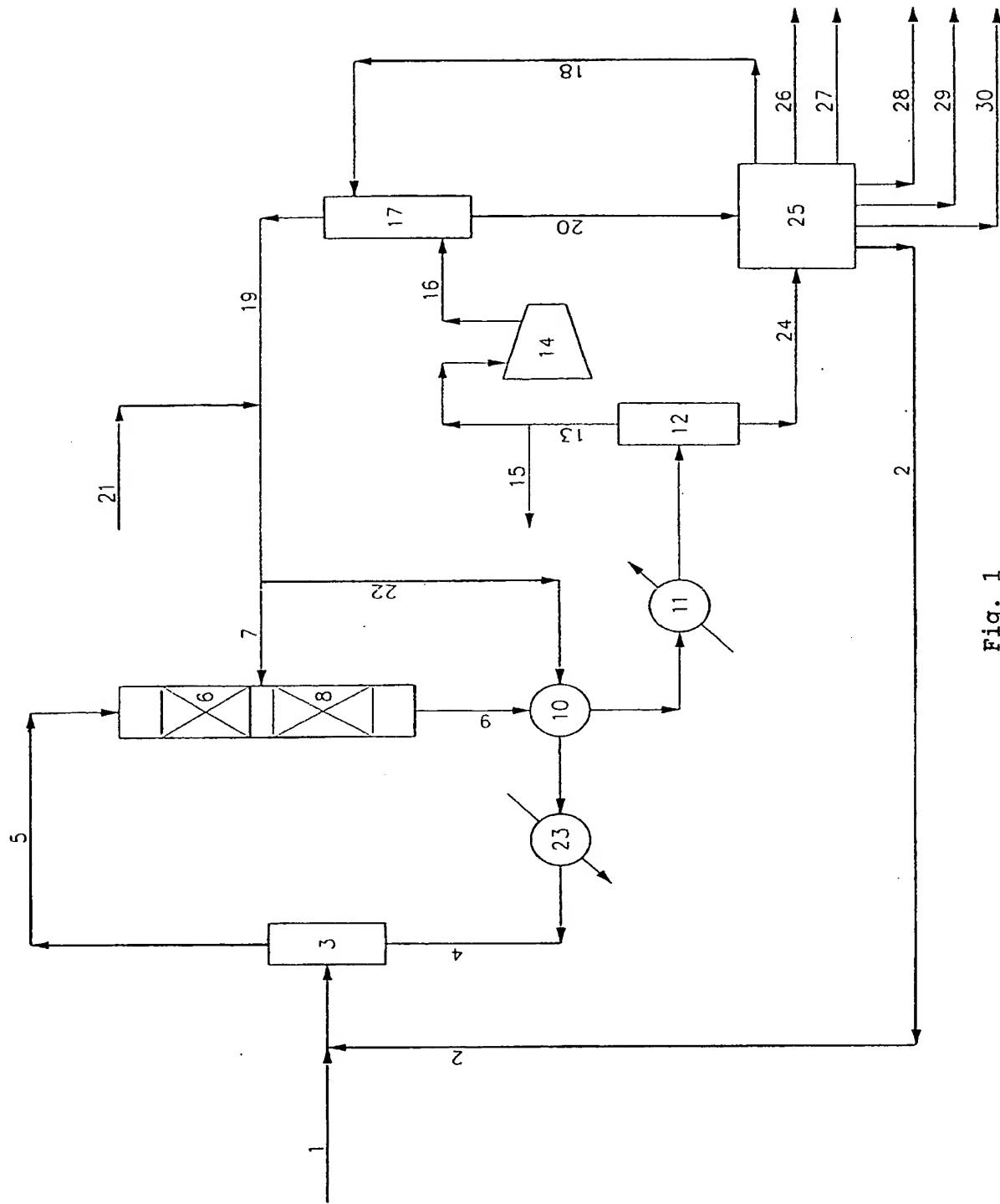


Fig. 1

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/EP 99/00013

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 6 C07D307/08 C07D307/32

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 97 43234 A (HILES ANDREW GEORGE ;TUCK MICHAEL WILLIAM MARSHALL (GB); KVAERNER) 20 November 1997 see page 4, line 24 – page 9, line 9; claim 1 ---	1
A	US 4 105 674 A (DE THOMAS WALDO ET AL) 8 August 1978 see page 1 see column 5, line 7 – line 56 ---	1
A	WO 86 07358 A (DAVY MCKEE LONDON) 18 December 1986 cited in the application see abstract see claims 1,2,4,7 ---	1

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

° Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority, claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

28 May 1999

Date of mailing of the international search report

07/06/1999

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl.  
Fax: (+31-70) 340-3016

Authorized officer

Paisdor, B

**INTERNATIONAL SEARCH REPORT**Inte. ~~rn~~ International Application No

PCT/EP 99/00013

**C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT**

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 322 140 A (STANDARD OIL CO OHIO) 28 June 1989 cited in the application see abstract; claim 1 see page 3, line 5 - page 5, line 30 -----	1

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No  
PCT/EP 99/00013

Patent document cited in search report		Publication date		Patent family member(s)		Publication date
WO 9743234	A	20-11-1997	AU	2782097 A		05-12-1997
US 4105674	A	08-08-1978	US	4083809 A		11-04-1978
WO 8607358	A	18-12-1986	BR	8606710 A		11-08-1987
			EP	0223814 A		03-06-1987
			JP	7053723 B		07-06-1995
			JP	63500099 T		14-01-1988
EP 0322140	A	28-06-1989	AT	82572 T		15-12-1992
			CA	1327812 A		15-03-1994
			CN	1034541 A, B		09-08-1989
			DE	3876083 A		24-12-1992
			ES	2052748 T		16-07-1994
			JP	1865909 C		26-08-1994
			JP	2000786 A		05-01-1990
			US	4965378 A		23-10-1990
			US	5072009 A		10-12-1991

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- BLACK BORDERS**
- IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- FADED TEXT OR DRAWING**
- BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- SKEWED/SLANTED IMAGES**
- COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- GRAY SCALE DOCUMENTS**
- LINES OR MARKS ON ORIGINAL DOCUMENT**
- REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- OTHER:** \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.